International Journal of Scientific Research and Management (IJSRM)
||Volume||12||Issue||06||Pages||144-160||2024||
Website: https://ijsrm.net ISSN (e): 2321-3418
DOI: 10.18535/ijsrm/v12i06.c04

A review: Modified biochar as an adsorbent for phosphorus removal from water

Aodi Tian[a], Hein Min Htet[a], Xulin Zhang[a], Zhaofeng Hu[a], Haozhen Zhang[a], He Huang[a,b,*]

[a]College of Chemistry and Environmental Engineering,Yangtze University,Jingzhou 43403,China
[b]Hubei Engineering Research Centers for Clean Production Control Of Oil and Gas Fields,Jingzhou 434023, China

Abstract:
In recent years, eutrophication of water bodies has become increasingly severe due to the rising content of phosphorus in these bodies. This escalation adversely affects the normal growth of aquatic organisms, leading to the deterioration of water quality, and ultimately impacting human life. Phosphorus removal is a crucial direction for addressing water body pollution. Therefore, it is of utmost importance to identify efficient, affordable, and feasible methods for removing phosphorus from wastewater. Adsorption, owing to its simplicity, efficiency, and low cost, is widely employed in water treatment. Biochar, in particular, is extensively used due to its high efficiency, renewability, low cost, and the ready availability of raw materials. This paper reviews the preparation methods of biochar and modified biochar, analyses the effects of pyrolysis temperature, solution pH, reaction temperature, adsorbent dosage, adsorption time and co-existing ions on the phosphorus removal of biochar materials. It also explores the necessity of desorption and regeneration of biochar, along with the prospects of biochar in the future of phosphorus removal.

Keywords: Biochar; Mechanism; Modified ;Performance; Removal

Highlight:

- The preparation methods of biochar and modified biochar are summarized in this paper.
- The influencing factors in the adsorption process, such as pH, temperature, dosage, reaction time and co-existing ions, were summarized.
- The main reaction mechanism of phosphate adsorption was summarized in this paper.

Phosphorus is one of the essential nutrients for the growth of all organisms, playing a vital role in both agricultural and industrial systems (Fan et al., 2022).In recent years, with the development of the economy, human activities have become more frequent, leading to increased discharge of pollutants into the water. Among these pollutants, the discharge of phosphorus results in the rapid growth of algae and other plankton in the water body, causing eutrophication. This process decreases the level of dissolved oxygen in the water, deteriorates water quality, and even leads to the death of fish and other organisms in large quantities, disrupting the ecological balance of the water (Zhang et al., 2020a).Eutrophication of water bodies is one of the common environmental problems faced by the world at present, caused by the excessive increase of nutrients in the water body. Common nutrients include elements such as phosphorus(Liu et al., 2022).Generally speaking, eutrophication of water bodies is highly related to anthropogenic factors, such as the use of phosphorus-containing laundry detergents and the discharge of industrial wastewater. In aquatic environments, phosphorus can exist in a variety of forms, including orthophosphates ,polyphosphates, and organic phosphorus. Orthophosphate is the form most readily taken up by plants and is therefore the target of efforts to remove and recover it from water(Zhi et al., 2022).

At present, the commonly used technologies for treating phosphorus-containing wastewater include biological method, chemical precipitation method, adsorption method, ion exchange method and membrane separation method. The biological removal of phosphorus can be divided into two categories. The first is the traditional biological phosphorus removal, where polyphosphorus bacteria release phosphorus under anaerobic conditions. Subsequently, in aerobic conditions, excess phosphorus is absorbed, and the purpose of biological phosphorus removal from wastewater is achieved through the discharge of phosphorus-rich sludge. The second category is denitrification phosphorus removal. Under anaerobic conditions, denitrification by polyphosphorus bacteria releases phosphorus. Then, in anoxic reaction conditions, phosphorus is excessively absorbed through the use of electron receptors. Under the reaction conditions, excess phosphorus is absorbed and nitrate ammonia is reduced to nitrogen, achieving the goals of both biological phosphorus removal and denitrification of wastewater (Gao et al., 2023).Despite the low operating cost of the biological method for phosphorus removal, its operational effectiveness remains unstable. Chemical precipitation method involves adding chemicals to form insoluble phosphate precipitates. Subsequently, solid-liquid separation is employed to remove phosphorus from the wastewater. The chemicals commonly used for phosphorus precipitation mainly includes iron salts, aluminum salts and calcium salts, falling into the three categories (Kang et al., 2017).These salts are effective in precipitating dissolved phosphorus components, promoting the formation of larger particles and agglomerates (Reif et al., 2023).While the chemical precipitation method for phosphorus removal is stable, reliable, and efficient, it comes with a high economic cost. Additionally, it generates a large amount of chemical sludge with a complex composition, making it difficult to manage and prone to causing secondary pollution. This aspect is not conducive to achieving phosphorus recovery and resource utilization. The adsorption method involves adding specific adsorbents to wastewater,where active groups bond with phosphorus to achieve removal. This process allows for both the removal and recovery of phosphate simultaneously. On the other hand, ion exchange method of phosphorus removal relies on exchanging ions and PO_4^{3-} in sewage(Zhang et al., 2023b).While effective,the ion exchange method has limitations in terms of exchange capacity. The membrane separation method is a technology that leverages the pore size of the membrane and electrostatic effects.This allows for the selective permeability of different ions under external force,effectively separating phosphorus from solvents in wastewater(Papadopoulou et al., 2023).The operation of membrane technology for phosphorus removal is often constrained by both the characteristics of the membrane and the characteristics of the wastewater.

The adsorption method can reduce the generation of subsequent sludge, offering a low-cost operation. As a result, the adsorption method for phosphorus removal has gradually emerged as a technology with promising application prospects. The key to the success of the adsorption method lies in developing materials with a strong adsorption effect and minimal risk of secondary pollution. In practical applications, it is common to combine multiple methods to achieve higher treatment efficiency. Table 1 shows the adsorption effects of different adsorbents on pollutants.

Table 1 Adsorption effect of different adsorbents on pollutants

Absorbent material type	Absorbent material		Modification method	Adsorption efficiency	Reference s
Biomass-based adsorbent materials	Sludge	Activated sludge	Mixing of sludge,eggshells and oyster shells by ball milling	154.18 mg/g	(Li et al., 2023b)
	Agricultural solid waste	Pomegranate arils	Load La、Fe	78.99 mg/g	(Akram et al., 2021)
		Crab Shells	Load Fe	149.27 mg/g	(Xu et al., 2023b)
		Tangerine peel	Load Zn、Ca	52.96 mg/g	(Chen et al., 2022)
		Rice straw	Load La、Ca	84.72 mg/g	(Zhang et al., 2023a)
		Corn Stalks	Load Mg	221.89 mg/g	(Li et al., 2022a)
		Tea leaves	loaded zero-valent iron (physics)	186.2mg/g（Cr）	(Rajput et al., 2023)
		Bagasse	Chitosan biopolymers	37.2 mg/g	(Manyatshe et al., 2022)
		Rice husk	Introduction of the xanthate group	90.02 mg/g（Crystal violet dye）	(Homagai et al., 2022)
	Industrial solid waste	Cinder	Load La 、Mg	39.22 mg/g	(Yang et al., 2023)
		Slag	Wet ball mill pyrolysis	39 mg/g	(Zhou et al., 2023)
		Fly ash	Preparation of mesontobermullite	221.2 mg/g	(Wang et al., 2022)

Biochar not only reduces the cost of remediation but also enables the resourceful use of waste (Liu et al., 2023a).Biomass-based adsorbent materials are widely used because of their renewable, sustainable energy, low cost, and easy availability of raw materials (Luo et al., 2020).Biochar-based adsorbent materials are mainly sludge, industrial solid wastes such as steel slag, fly ash, etc.,and agricultural solid waste a such as straw ,rice husk ,etc..

1 Preparation of biochar

Biochar is a porous ,carbon-rich material produced from biomass under high temperature and oxygen-limited conditions (Li et al., 2023a).However, the optimal temperature for the preparation of each biochar varies depending on the feedstock used.Various methods are employed for biochar preparation,typically including high temperature cracking,gasification pyrolysis,hydrothermal carbonization and microwave thermal cracking.

1.1 High temperature cracking

High-temperature cracking is the process of pyrolyzing biomass materials at elevated temperatures in an oxygen-deprived environment to obtain products with different physicochemical properties (Bardi et al., 2023).Manmeen et al (Manmeen et al., 2023) investigated the conversion of durian peels to biochar through slow pyrolysis. The analysis revealed that only the pyrolysis temperature significantly influenced biochar and pyrolyte yields. As the pyrolysis temperature increased, the biochar yield decreased, and the pyrolyte yield increased. This was primarily due to the temperature increase promoting the thermal decomposition of durian peel to produce gaseous products.

1.2 Hydrothermal carbonisation

Hydrothermal carbonisation is the process of thermally decomposing organic matter into biochar in a closed system with the presence of water at a certain temperature and autogenous pressure. This method is regarded as a highly promising technology for biochar treatment (Li et al., 2020),enabling the development of functional materials with economic benefits in an environmentally friendly process. The hydrothermal carbonisation method can control the particle size, morphology and surface functional groups of the carbonaceous material(Yun et al., 2022).This control enhances the surface area and porosity of the biochar, making it conducive to adsorption (Wu et al., 2020).Stelgen et al (Inkoua et al., 2022) investigated the pyrolysis of furfural residue (FR),a solid waste from the production of furfural from corn kernels, at different heating rates in the range of 350 ~ 650 °C .The results revealed that, owing to the high ash content of FR,the derived bio-oil was rich in cellulose- and lignin-derived organic matter. The organic components easily underwent cracking, resulting in the formation of biochar and gas. Higher pyrolysis temperatures favored the formation of organic matter with a molten ring structure. Additionally, lower heating rates during pyrolysis led to the production of biochar with increased thermal stability and a higher fixed carbon content, achieved by enhancing the degree of deoxygenation.

1.3 Gasification pyrolysis

Gasification pyrolysis is a side reaction in high-temperature gasification, producing material char (Inkoua et al., 2022).Xin et al (Xin et al., 2017) proposed a two-step gasification process for treating cattle manure, studying for the first time the impact of temperature on product distribution and biochar properties in the pyrolysis-carbonization process. It was observed that with prolonged holding time, especially at high temperatures, a portion of heavy hydrocarbons underwent a secondary cracking reaction. Both temperature and holding time exhibited a synergistic effect on the products and mechanism of the pyrolysis-carbonation process. Additionally, as carbonization temperature increased, the surface of the biochar displayed unevenness with multiple cracks and pores in the bulk structure, attributed to the precipitation of volatile components in the pyrolysis-carbonation process.

1.4 Microwave Thermal Cracking

Microwave heating method can achieve more uniform heat distribution, higher heating rates and higher temperatures than conventional heating methods. This is because heat is generated inside the core of the target material during microwave heating, as opposed to external heat source. This improvement enhances the quality of pyrolysis products (Xu et al., 2022).On the other hand, the instantaneous control characteristic of microwave heating reduces the thermal inertia of the equipment and improves the control of the heating power. This feature allows for the rapid optimization of the synthesis conditions(Shen et al., 2022).Zhang et al (Zhang et al., 2022) used microwave technology to prepare porous carbon from pyrolysis residue of chilli straw.The study revealed that the thermal stability of biochar increased with the rise of pyrolysis temperature, and the specific surface area of biochar also increased accordingly. The porous char prepared by microwave heating exhibited better electrical properties than conventional heating, and the biochar obtained at higher pyrolysis temperatures had a richer pore structure after activation.

2 Preparation of modified biochar

While biochar possesses some adsorption capacity, it is limited, necessitating modification to enhance its adsorption effectiveness (Ambika et al., 2022).Modified carbonaceous adsorbents exhibit significantly higher adsorption capacities for phosphate compared to unmodified adsorbents. This is attributed to the inherent negative charge of most raw carbonaceous adsorbents, which is not conducive to the adsorption of negatively charged phosphate ions. Commonly used modification methods include physical modification, chemical modification, and biological modification.

2.1 Physical modification

Physical modification primarily entails creating additional microporous and mesoporous structures on the surface through processes such as microwave radiation and ball milling.This aims to increase the specific surface area of biochar and enhance its adsorption performance(Huang et al., 2021).The physical modification method is environmentally friendly as it does not involve the use of any chemicals. Microwave radiation involves the emission of energy from the inside out creating an obvious temperature difference inside the biochar. This process induces irregular expansion and contraction promoting the formation of the pore structure of biochar (Lin et al., 2022).On the other hand,the ball mill technique destroys chemical bonds and reduces particle size, effectively increasing the specific surface area of biochar This innovative method is easy environmentally friendly, economical, fast and solvent-free(Lyu et al., 2018).

2.2 Chemical modification

Chemical modification is a common method because it directly affects the surface chemical properties of biomass or biochar. Examples include acid-base modification, oxidation methods metal loading and others.

The acid and alkali modification method involves treating biochar with acid or alkali to alter its specific surface area. This introduces carboxyl and hydroxyl groups thereby changing the type and number of surface functional groups. These modifications aim to improve the adsorption performance of the biochar Commonly used acids for this method include HCI,H_2SO_4,HNO_3,etc.,and commonly used alkalis are NaOH, KOH, etc..

Oxidation modification generally involves using oxidants as modifiers to enhance the adsorption performance of biochar. Commonly used oxidants include H_2O_2,$KMnO_4$,and so on.The metal loading method involves soaking biochar in metal ions, resulting in a larger surface area and active adsorption sites.Since the surface of biochar is often rich in oxygen, nitrogen, sulfur, and other functional groups, it tends to have a negatively charged surface, which is not conducive to the adsorption of anions.The modification of biochar with metals can alter surface properties, such as surface area, surface charge, pore size,and functional groups Therefore, the use of metal cations can shift the surface charge of biochar from negative to positive, filling the pores with metal ions.This modification increases the porosity of the biochar,thereby improving its adsorption capacity for phosphate (Shakoor et al., 2021). Commonly used modified metals include Mg,Fe, and La.As metal ions are magnetic, their presence can improve the recycling rate of biochar to some extent.

2.3 Biomodification

Biomodification is mainly a method of combining microorganisms with certain functions with biochar to improve its physicochemical properties, specifically low cost and high removal rate (Li et al., 2022b). Table 2 shows the adsorption effects of different modification methods on pollutants.

Table 2 Adsorption effect of different modification methods on pollutants

Modification method		Materials	Adsorption efficiency	References
Physical modification	Ball milling	Corn Stover	329 mg/g	(Ai et al., 2023)
		Walnut shells	2750 mg/g（Petroleum pollutants)	(Wei et al., 2023)
	Microwave radiation	Biosolids in clay settling ponds	147mg/g	(Antunes et al., 2018)
		Teak waste	66.69 mg/g（Methylene blue）	(Firdaus Mohamad Yusop et al., 2022)
Chemical modification	Acid modification	Corncob（H_2SO_4）	221.1mg/g（Na^+）	(Yu et al., 2023)
		Wheat straw（HNO_3）	46.18 mg/g（Cd）	(Zheng et al., 2021)
	Alkali modification	Lycium barbarum branches（KOH）	769mg/g（Methylene blue）	(Liu et al., 2023b)
	Oxidation modification	Hickory Chips（H_2O_2）	310mg/g（Methylene blue）	(Zhang et al., 2021)
		Hickory nutshell,bamboo,wheat straw（$KMnO_4$）	189.24 mg/g（Pb）	(Zhang et al., 2023c)
	Modified by metal loading method	Chitosan（La、Al）	264.48mg/g	(Lan et al., 2022)
		Corn stove r（Ca）	33.944 mg/g	(Zhuo et al., 2022)
		Wood chips (Ca、Al、La)	152.9 mg/g	(Cheng et al., 2023)
Biological modification		Attapulgite (Silicate bacteria)	9.54mg/g	(Xu et al., 2023a)

3 Factors affecting the adsorption effect

The effectiveness of pollutant removal depends on both the nature of the adsorbent and the environmental conditions in which it operates.The adsorbent's intrinsic properties,such as surface area,porosity,and chemical composition,play a crucial role in determining its capability to attract and retain pollutants.Simultaneously,the specific conditions of the surrounding environment,including temperature,pH,and the concentration of pollutants,influence the adsorption process.This interplay between the adsorbent's characteristics and the environmental conditions highlights the importance of tailoring adsorption methods to specific pollutants and scenarios.Understanding and optimizing these factors are essential for designing efficient and sustainable pollutant removal systems.

3.1 Pyrolysis temperature

The physicochemical properties of biochar vary greatly with the feedstock and pyrolysis temperature (Wang and Yao, 2023).Pyrolysis temperature not only influence the surface properties of biochar,but also affects its yield.In general,,higher pyrolysis temperatures result in an increased number of voids in biochar,a larger specific surface area,and a stronger adsorption effect However,if the pyrolysis temperature is excessively high,it may lead to the destruction of the biochar's pore structure,consequently affecting its adsorption efficiency.Therefore,finding the most suitable pyrolysis temperatures for different biochar is essential (Zhang et al., 2020b).The organic fraction of biomass consists of three main components:cellulose,hemicellulose and lignin.Under the same pyrolysis conditions,different biomass feedstocks will yield biochar with varying physicochemical properties(Qiu et al., 2022).Different types of biochar possess distinct characteristics such as pore numbers and surface areas,leading to varied adsorption effects on phosphorus in water.Lignin exhibits a broader decomposition range,starting from lower temperatures and extending to higher temperatures than cellulose,while hemicellulose is more susceptible to thermal decomposition than cellulose(Faleeva et al., 2022).Given the often lower quality of biomass pyrolysis products,catalysts become crucial for improving their quality.In this regard,Ge et al (Ge et al., 2023) investigated additives and catalysts to enhance the quality of biomass pyrolysis products.They introduced appropriate amounts of Fe to carbon nanotubes prepared under conventional pyrolysis conditions and observed that the addition of 10% Fe inhibited the decomposition of functional groups on the surface of lignin while promoting the decomposition of functional groups on the surface of hemicellulose.Simultaneously,diffraction peaks attributed to carbon deposition were observed on the surface of Fe powder.Lignin biochar is characterized by a substantial number of pores,with the pore count increasing upon the addition of iron.Li et al(Li et al., 2023a) explored the impact of pretreatment temperature on the composition and properties of pyrolysis products,focusing particularly on biochar obtained at high temperatures.The study revealed that roasting cellulose from 170°C to 350°C had minimal effects on the total yield of biochar and bio-oil.However,calcination of cellulose at 260°C induced significant structural changes,favoring subsequent cleavage to produce anhydrous sugars and unsaturated oxygenated organics.Furthermore,the study found that cellulose crystals were completely removed at 350°C,forming graphitic carbon.

3.2 Solution pH

The pH level not only influences the surface charge of metal oxide composites but also dictates the form of phosphorus in an aqueous solution.Phosphorus in water primarily exists in four main forms:H_3PO_4,$H_2PO_4^-$,HPO_4^{2-} and PO_4^{3-}.As the pH increases,there is a transition from H_3PO_4 to $H_2PO_4^-$.The proportion of H_3PO_4 decreases with rising pH,while the proportion of $H_2PO_4^-$ increases,reaching a peak of 99% at pH 5.Concurrently,$H_2PO_4^-$ undergoes further conversion to HPO_4^{2-}.This transformation mirrors the shift from H_3PO to $H_2PO_4^-$.At pH 10,97.9% of phosphorus exists in the form of HPO_4^{2-}.With increasing pH,especially in strongly alkaline environments,phosphorus primarily exists in the form of PO_4^{3-}(Fan et al., 2022).Under acidic conditions,excess hydrogen ions can protonate the active adsorption sites,causing the biochar to behave as a weak acid,functioning as an electron acceptor,while the phosphate ion acts as a weak base.Conversely,under alkaline conditions,excess hydroxide groups deprotonate the active adsorption sites on the biochar's surface,making the biochar act as a weak base,and the phosphate ion behaves as a weak acid.Liang et al(Liang et al., 2023) developed an in-situ activation method based on the pyrolysis technique of $Mg(NO_3)_2$ activation,resulting in Mg-biochar adsorbents with abundant fine pores and active sites.The results indicated that the adsorption of $Mg(NO_3)_2$ on biochar was highly dependent on the initial pH of the solution.The maximum adsorption of phosphate nearly doubled as the pH increased from 3 to 9,but significantly decreased when the pH was raised to 13.

3.3 Reaction Temperature

During the adsorption process, temperature influences particle diffusion. An increase in temperature accelerates molecule diffusion and the frequency of intermolecular collisions,thereby enhancing the rate of precipitation reactions. Elevated temperature also augments the pore volume and porosity of the adsorbent, facilitating the entry of pollutant molecules to the inner pore surface. However, it's important to note that a higher reaction temperature is not always better. Excessively high temperatures may lead to the desorption of already adsorbed phosphate. Wang et al (Wang et al., 2016), in their lanthanum phosphorus adsorption experiments using oak chips, discovered that a higher adsorption temperature contributes to an improved adsorption capacity for phosphate. As the temperature increased from 15 ℃ to 45 ℃,the amount of phosphate adsorption rose from 43.70 mg/g to 60.1 mg/g.This phenomenon can be attributed to the intensified random thermal movement of ions in the solution at higher temperatures, enhancing the likelihood of collision between adsorption sites and phosphate ions.

3.4 Adsorbent dosage

In the process of removing phosphorus pollutants from water using biochar as an adsorbent,the dosage of the adsorbent is one of the most critical factors influencing the adsorption effect.Selecting the optimal dosage of the adsorbent not only conserves resources but also enhances its utilization.Theoretically,as the adsorbent dosage increases,the number of adsorption sites also increases,leading to an improvement in the adsorption effect.However,this theoretical expectation is not always realized in practice.Studies have demonstrated that when the dosage of biochar reaches a certain threshold,its adsorption capacity exhibits only a minimal increase or remains unchanged with further dosage increments.This phenomenon can be attributed to the rise in active adsorption sites as the dosage of the adsorbent increases.Consequently,the occupancy of active sites on a unit mass of adsorbent decreases,resulting in a decline in adsorption capacity (Li et al., 2023c).Sisay et al(Begna Sisay et al., 2023),in their investigation of phosphate adsorption by Mg/Zr modified nano-biochar extracted from waste coffee grounds,observed that the removal rate increased with the rise in adsorbent dosage,reaching a maximum at an adsorbent dosage of 40 mg.However,the removal rate started to decrease when the adsorbent dosage exceeded 40 mg.This phenomenon can be interpreted as an outcome of the increased dosage of adsorbent,leading to a rise in adsorbent surface area and the availability of additional adsorption sites.Nevertheless,with a further increase in adsorbent dosage,the particles tended to aggregate,reducing their interaction with anions.

3.5 Reaction time

The role of reaction time in the adsorption process is crucial.Over time,the adsorption rate accelerates until the adsorbent surface becomes saturated,at which point the adsorption rate slows down to reach saturation (Qu et al., 2023).Zeeshan et al (Ajmal et al., 2018) studied on the adsorption,desorption,and regeneration characteristics of ferric iron hydrate,acicular ferrite,and magnetite on phosphates,experiments investigating the effect of reaction time on adsorption revealed that the rate of phosphorus adsorption generally increased with time.However,after a rapid adsorption period of 0 to 120 minutes,the adsorption rate of the tested substances slowed down and eventually saturated.This saturation occurred because,at this point,the surface of the biochar had become saturated,limiting its capacity to receive more pollutants.

3.6 Co-existing ions

When utilizing adsorption for the treatment of actual wastewater,the substantial presence of anions in the wastewater can adversely impact phosphorus removal,including NO_3^-,Cl^-,SO_4^{2-},HCO_3^-,etc.In addressing this challenge,Song et al(Song et al., 2023) quaternised rice straw and loaded it with $La(OH)_3$ nanoparticles to create composites with an excellent affinity for phosphates (AM-La).The adsorption capacity of phosphate by AM-La saw a significant increase by 116-125% even in the presence of high nitrate concentration.Additionally,AM-La demonstrated remarkable selectivity for phosphate in the presence of anions such as Cl^-,HCO_3^- and SO_4^{2-}.The main mechanism driving phosphate removal by AM-La was the synergistic effect of ion exchange,electrostatic attraction,and ligand exchange,leading to the formation of lanthanum phosphate.This was substantiated through characterization conducted before and after AM-La adsorption.The results of adsorption/desorption studies involving phosphate in the presence of coexisting ions and real water samples indicate that AM-La exhibits excellent regeneration capability,showcasing its potential for practical applications.

4 Desorption and regeneration of biochar

Phosphate, being a non-renewable natural resource, can be effectively recovered through its adsorption from wastewater,addressing the future demand for this essential element. However, after reaching adsorption saturation,the adsorbent experiences a reduction in pore number and available specific surface area, thereby influencing subsequent adsorption effectiveness. The regeneration of biochar stands out as an ecologically sound,safe,sustainable,and maximally beneficial approach. Gradually gaining cost-effectiveness, finding an advanced resolving agent with commendable adsorption and desorption properties holds the potential to significantly reduce the overall cost of adsorbents.

Currently,the primary methods employed for the recovery and regeneration of adsorbents include magnetic separation,filtration,thermal desorption,and chemical desorption.

Magnetic separation,involving the introduction of metal nanoparticles,is utilized for adsorbent recovery.The maximum adsorption of Pb^{2+} in wastewater system was 58.5 mg/g by magnetic chitosan-clayite prepared by Rusmin et al (Rusmin et al., 2022).The removal of Pb^{2+} was 82% after 4 magnetic regenerations.Liang et al (Liang et al., 2022) synthesized metallic carbon containing carbon nanotubes and cobalt nanoparticles,employing it for the removal of ofloxacin antibiotic.The adsorption capacity reached up to 118.3 mg/g and maintained more than 97% efficiency after four magnetic regenerations.Filtration,considered the simplest and most direct method for adsorbent recovery,is easier to implement compared to nano-biochar,which typically has a larger particle size (Baskar et al., 2022).The thermal desorption method involves heating the adsorbent to a specific temperature,breaking the bond between the adsorbent and the contaminant (Momina et al., 2018).Toński et al (Toński et al., 2021) conducted a study on the thermal and chemical regeneration of multi-walled carbon nanotubes at 300°C with a holding time of 2 h.The results indicated that a higher temperature led to a greater loss of multi-walled carbon nanotubes.However,the adsorption capacity remained unaffected even after five contamination-thermal regeneration cycles.Chemical desorption is the use of organic or inorganic solvents to remove or wash off the contaminants from the adsorbent(Gupta et al., 2020),thereby maintaining the adsorption capacity and allowing for reuse.Khenniche et al (Khenniche et al., 2021) prepared ferromagnetic carbon from coffee grounds and employed it as an adsorbent for removing tetracycline from a wastewater system.Chemical regeneration with 0.1 M NaOH resulted in 72% and 40% adsorption for fresh and spent carbon,respectively.Siciliano et al (Siciliano et al., 2021) used 1M HCl for regeneration in an experiment to study the adsorption effect of thermal plasma expanded graphite on methylene blue.After five regenerations,the adsorption efficiency of the dye was 87%.

5 Adsorption mechanism

The reaction mechanism and adsorption efficiency are highly dependent on the adsorbent's performance. Biochar employs various adsorption mechanisms, including electrostatic attraction, ion exchange, surface complexation, ligand exchange, hydrogen bonding, physical adsorption,chemisorption(Gizaw et al., 2021).

Electrostatic attraction refers to the long-range electrostatic force between the adsorbent and phosphate ions.During adsorption,the protonated surface of the adsorbent attracts phosphate ions,which are negatively charged.The zero-point charge serves as a crucial indicator reflecting the electrostatic effect of biochar.Modification can alter the zero-point charge of biochar,thereby influencing its electrostatic effects.Liu et al (Liu et al., 2021) found that the zero-charge point of biochar was about 7.8 in the experiments to study the adsorption of phosphate by nanoscale-loaded zero-valent iron biochar,when the pH was low,the main form of phosphorus in the liquid phase was H_3PO_3,which was unfavourable for the interaction site with positive ions,which resulting in low adsorption capacity.The optimal solution pH for adsorption of PO_3-P is 7~9.When pH>9,the electrostatic repulsion between PO_3-P and biochar is getting stronger and stronger,resulting in the decrease of PO_3-P adsorption capacity.Ions were exchanged between the solution and the insoluble solid adsorbent through an ion exchange process.Throughout the reaction process,various functional groups attach to the adsorbent's surface through different modification methods,influencing phosphate adsorption via ion exchange.Surface complexation typically involves two mechanisms:outer-sphere complexation and inner-sphere complexation.In the outer-sphere complexation mechanism,electron transfer occurs between the chemicals.They remain separate before,during,and after the electron transfer,without forming intermediates or breaking chemical bonds.In the inner-sphere complexation mechanism,electron transfer occurs between the complexes through bridging ligands and covalent bond formation (Priya et al., 2022).Intrasphere complexes and electrostatic attraction between positively charged metal and metal oxide surfaces and negatively charged phosphate ions can produce ligand exchange(Shi et al., 2019).In ligand exchange,the ligands,typically ions or natural molecules,play a crucial role.Hydrogen bonds form between hydrogen-containing and oxygen-containing groups.During adsorption,the positively charged hydrogen attracts the negatively charged oxygen ions of phosphate,forming a phosphate crystal structure and facilitating phosphorus removal.If phosphate ions are solely adsorbed through van der Waals forces,the mechanism involved is physical adsorption.The physical adsorption process is straightforward,with relatively low adsorption capacity and weak bonding forces,facilitating the regeneration of the adsorbent.In their study on the adsorption effects of a magnesium-doped biochar/bentonite composite ball,Xi et al (Xi et al., 2022) found that biochar was modified through coprolysis to increase the specific surface area and total volume.The introduction of magnesium particles into the biochar's pore space enhanced the adsorption of nitrogen and phosphorus.In chemisorption,chemical bonds form between the adsorbent and phosphate ions,involving the transfer,exchange,or sharing of electrons between the adsorbent and phosphate ions.Jiang et al(Jiang et al., 2019) utilized taro stover,maize stover,cassava straw,cedar straw,banana straw,and oil tea husk as raw materials for the adsorption of phosphorus in aqueous solution.The primary adsorption mechanisms involve surface electrostatic attraction,Mg^{2+} precipitation,and complexation with surface hydroxyl groups.

The adsorption mechanism varies among different biocarbon materials,particularly modified materials.Lesaoana et al (Lesaoana et al., 2019) impregnated Hawaiian activated carbon with varying concentrations of sulfuric,nitric,and phosphoric acids (20-60% v/v) and subjected it to heat in a muffle furnace.This was done to enhance the structural properties of the adsorbent and improve the removal of Cr(VI).Functional groups such as CN,NO,sulphur and phosphorus were introduced during this process and Fourier transform infrared spectroscopy showed the presence of CN,NO,sulphur and phosphorus peaks at 1213,1531,1204 and 1214 cm^{-1} ,respectively,demonstrating that the acid treatment resulted in the effective attachment of functional groups.The surface area of raw biochar increased from 545 m^2 /g to 824 m^2 /g after acid treatment.The optimum adsorption performance for Cr(VI) after 120 min of contact reaction was 98% at pH 1 and 93% at pH 4.Compared to raw carbon (22.3 mg/g),the adsorption capacity was increased to 40.99 mg/g with 220% (v/v) HNO_3 activator and decreased to 9.66 mg/g with 20% (v/v) H_2SO_4 activator.Jian et al(Jian et al., 2020) found that the mechanism of adsorption of phosphate ions in the characterization of iron-modified biochar mainly involved electrostatic interactions,the presence of hydroxyl and carboxyl groups and protonation of iron oxide resulted in a positively charged surface,and this positive charge contributed to the electrostatic attraction of negatively charged PO_4^{3-} ions to the surface of the biochar,leading to adsorption.Jiang et al(Jiang et al., 2021) prepared magnesium-modified multi-walled carbon nanotubes as a novel adsorbent for the recovery of phosphate from wastewater,and the maximum experimental adsorption up to 198 mg P/g.Magnesium modified biochar presents a positively charged surface in solution due to the protonation of magnesium oxide.This positive charge produces a strong affinity for negative ions,leading to PO_4^{3-} ion adsorption,and the adsorbed phosphate ions form $Mg_3(PO_4)_2$ precipitation,which is the main adsorption mechanism of magnesium-modified biochar.Deng et al (Deng et al., 2021)prepared a calcium-modified chitosan microsphere for adsorption of phosphate from simulated wastewater by in situ precipitation method.The results showed that the main adsorption mechanism was co-precipitation,where PO_4^{3-} ions were adsorbed by Ca^{2+} on Ca-modified biochar,leading to the formation of the product hydroxyapatite.Luo et al (Luo et al., 2024) synthesised lanthanum-modified natural zeolite for adsorption of phosphorus by precipitation and hydrothermal methods,and the results showed that this adsorbent had an adsorption capacity of 122.7 mg/g,with good phosphorus adsorption and passivation capacity,exceeding most lanthanum-modified materials.Characterisation showed that intrasphere complexation and electrostatic attraction were the main mechanisms promoting phosphate adsorption.

Typically,the removal of pollutants involves the simultaneous operation of multiple mechanisms.Various processes,such as electrostatic attraction,ion exchange,surface complexation,ligand exchange,hydrogen bonding,physical adsorption,and chemisorption,may collaboratively contribute to the overall effectiveness of pollutant removal.

6 Conclusions

As a simple, readily available, and environmentally friendly material, biochar holds significant potential for widespread application in water treatment. However, certain challenges still need addressing for further improvement:

(1) Enhancing the treatment efficiency of biochar or modified biochar in practical water treatment;

(2) Mitigating pollution during the preparation of modified biochar;common metals used in modification,such as magnesium and lanthanum,incur high costs and are prone to causing secondary pollution;

(3) Identifying more efficient biochar materials and refining modification methods to increase adsorption efficiency;

(4) Exploring more suitable desorption methods to enhance the regeneration capability of biochar.

References.

1. AI, D., MA, H., MENG, Y., WEI, T. & WANG, B. 2023. Phosphorus recovery and reuse in water bodies with simple ball-milled Ca-loaded biochar. Sci Total Environ, 860, 160502.
2. AJMAL, Z., MUHMOOD, A., USMAN, M., KIZITO, S., LU, J., DONG, R. & WU, S. 2018. Phosphate removal from aqueous solution using iron oxides: Adsorption, desorption and regeneration characteristics. J Colloid Interface Sci, 528, 145-155.
3. AKRAM, M., XU, X., GAO, B., WANG, S., KHAN, R., YUE, Q., DUAN, P., DAN, H. & PAN, J. 2021. Highly efficient removal of phosphate from aqueous media by pomegranate peel co-doping with ferric chloride and lanthanum hydroxide nanoparticles. Journal of Cleaner Production, 292.
4. AMBIKA, S., KUMAR, M., PISHARODY, L., MALHOTRA, M., KUMAR, G., SREEDHARAN, V., SINGH, L., NIDHEESH, P. V. & BHATNAGAR, A. 2022. Modified biochar as a green adsorbent for removal of hexavalent chromium from various environmental matrices: Mechanisms, methods, and prospects. Chemical Engineering Journal, 439.
5. ANTUNES, E., JACOB, M. V., BRODIE, G. & SCHNEIDER, P. A. 2018. Isotherms, kinetics and

mechanism analysis of phosphorus recovery from aqueous solution by calcium-rich biochar produced from biosolids via microwave pyrolysis. Journal of Environmental Chemical Engineering, 6, 395-403.

6. BARDI, M. J., MUTUNGA, J. M., NDIRITU, H. & KOCH, K. 2023. Effect of pyrolysis temperature on the physiochemical properties of biochar and its potential use in anaerobic digestion: A critical review. Environmental Technology & Innovation, 32.
7. BASKAR, A. V., BOLAN, N., HOANG, S. A., SOORIYAKUMAR, P., KUMAR, M., SINGH, L., JASEMIZAD, T., PADHYE, L. P., SINGH, G., VINU, A., SARKAR, B., KIRKHAM, M. B., RINKLEBE, J., WANG, S., WANG, H., BALASUBRAMANIAN, R. & SIDDIQUE, K. H. M. 2022. Recovery, regeneration and sustainable management of spent adsorbents from wastewater treatment streams: A review. Sci Total Environ, 822, 153555.
8. BEGNA SISAY, G., BELEGE ATISME, T., ADMASSU WORKIE, Y., WORKU NEGIE, Z. & LEUL MEKONNEN, M. 2023. Mg/Zr modified nanobiochar from spent coffee grounds for phosphate recovery and its application as a phosphorous release fertilizer. Environmental Nanotechnology, Monitoring & Management, 19.
9. CHEN, Z., WU, Y., HUANG, Y., SONG, L., CHEN, H., ZHU, S. & TANG, C. 2022. Enhanced adsorption of phosphate on orange peel-based biochar activated by Ca/Zn composite: Adsorption efficiency and mechanisms. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 651.
10. CHENG, F., WANG, Y., FAN, Y., HUANG, D., PAN, J. & LI, W. 2023. Optimized Ca-Al-La modified biochar with rapid and efficient phosphate removal performance and excellent pH stability. Arabian Journal of Chemistry, 16.
11. DENG, L., GUAN, Q., NING, P., HE, L. & ZHANG, D. 2021. Synthesis of 3D calcium-modified microspheres for fast purification of simulated phosphate wastewater. Journal of Water Process Engineering, 42.
12. FALEEVA, Y. M., LAVRENOV, V. A. & ZAICHENKO, V. M. 2022. Investigation of plant biomass two-stage pyrolysis based on three major components: cellulose, hemicellulose, and lignin. Biomass Conversion and Biorefinery.
13. FAN, X., WU, Y., HE, Y., LIU, H., GUO, J., LI, B. & PENG, H. 2022. Efficient removal of phosphorus by adsorption. Phosphorus, Sulfur, and Silicon and the Related Elements, 198, 375-384.
14. FIRDAUS MOHAMAD YUSOP, M., AZIZ, A. & AZMIER AHMAD, M. 2022. Conversion of teak wood waste into microwave-irradiated activated carbon for cationic methylene blue dye removal: Optimization and batch studies. Arabian Journal of Chemistry, 15.
15. GAO, M., SUN, S., QIU, Q., ZHOU, W. & QIU, L. 2023. Enrichment denitrifying phosphorus-accumulating organisms in alternating anoxic-anaerobic/aerobic biofilter for advanced nitrogen and phosphorus removal from municipal wastewater. Journal of Water Process Engineering, 55.
16. GE, L., ZHAO, C., ZUO, M., DU, Y., YAO, L., LI, D., CHU, H., WANG, Y. & XU, C. 2023. Effect of Fe on the pyrolysis products of lignin, cellulose and hemicellulose, and the formation of carbon nanotubes. Renewable Energy, 211, 13-20.
17. GIZAW, A., ZEWGE, F., KUMAR, A., MEKONNEN, A. & TESFAYE, M. 2021. A comprehensive review on nitrate and phosphate removal and recovery from aqueous solutions by adsorption. Journal of Water Supply: Research and Technology-Aqua, 70, 921-947.
18. GUPTA, S., SIREESHA, S., SREEDHAR, I., PATEL, C. M. & ANITHA, K. L. 2020. Latest trends in heavy metal removal from wastewater by biochar based sorbents. Journal of Water Process

Engineering, 38.
19. HOMAGAI, P. L., POUDEL, R., POUDEL, S. & BHATTARAI, A. 2022. Adsorption and removal of crystal violet dye from aqueous solution by modified rice husk. Heliyon, 8, e09261.
20. HUANG, W. H., LEE, D. J. & HUANG, C. 2021. Modification on biochars for applications: A research update. Bioresour Technol, 319, 124100.
21. INKOUA, S., LI, C., FAN, H., BKANGMO KONTCHOUO, F. M., SUN, Y., ZHANG, S. & HU, X. 2022. Pyrolysis of furfural residues: Property and applications of the biochar. J Environ Manage, 316, 115324.
22. JIAN, X., LI, S., FENG, Y., CHEN, X., KUANG, R., LI, B. & SUN, Y. 2020. Influence of Synthesis Methods on the High-Efficiency Removal of Cr(VI) from Aqueous Solution by Fe-Modified Magnetic Biochars. ACS Omega, 5, 31234-31243.
23. JIANG, S., WANG, J., QIAO, S. & ZHOU, J. 2021. Phosphate recovery from aqueous solution through adsorption by magnesium modified multi-walled carbon nanotubes. Sci Total Environ, 796, 148907.
24. JIANG, Y. H., LI, A. Y., DENG, H., YE, C. H., WU, Y. Q., LINMU, Y. D. & HANG, H. L. 2019. Characteristics of nitrogen and phosphorus adsorption by Mg-loaded biochar from different feedstocks. Bioresour Technol, 276, 183-189.
25. KANG, J., SUN, W., HU, Y., GAO, Z., LIU, R., ZHANG, Q., LIU, H. & MENG, X. 2017. The utilization of waste by-products for removing silicate from mineral processing wastewater via chemical precipitation. Water Res, 125, 318-324.
26. KHENNICHE, L., CHEMACHE, Z., SAIDOU-SOULEYMANE, M. & AISSANI-BENISSAD, F. 2021. Elimination of antibiotics by adsorption on ferromagnetic carbon from aqueous media: regeneration of the spent carbon. International Journal of Environmental Science and Technology, 19, 9571-9586.
27. LAN, Z., LIN, Y. & YANG, C. 2022. Lanthanum-iron incorporated chitosan beads for adsorption of phosphate and cadmium from aqueous solutions. Chemical Engineering Journal, 448.
28. LESAOANA, M., MLABA, R. P. V., MTUNZI, F. M., KLINK, M. J., EJIDIKE, P. & PAKADE, V. E. 2019. Influence of inorganic acid modification on Cr(VI) adsorption performance and the physicochemical properties of activated carbon. South African Journal of Chemical Engineering, 28, 8-18.
29. LI, D., LI, C., FAN, M., SHAO, Y., SUN, Y., ZHANG, L., ZHANG, S., HUANG, Y., LI, B., WANG, S. & HU, X. 2023a. Investigation of property of biochar in staged pyrolysis of cellulose. Journal of Analytical and Applied Pyrolysis, 172.
30. LI, J., CAO, L., LI, B., HUANG, H., YU, W., SUN, C., LONG, K. & YOUNG, B. 2023b. Utilization of activated sludge and shell wastes for the preparation of Ca-loaded biochar for phosphate removal and recovery. Journal of Cleaner Production, 382.
31. LI, L., CHEN, Q., ZHAO, C., GUO, B., XU, X., LIU, T. & ZHAO, L. 2022a. A novel chitosan modified magnesium impregnated corn straw biochar for ammonium and phosphate removal from simulated livestock wastewater. Environmental Technology & Innovation, 26.
32. LI, L., FLORA, J. R. V. & BERGE, N. D. 2020. Predictions of energy recovery from hydrochar generated from the hydrothermal carbonization of organic wastes. Renewable Energy, 145, 1883-1889.
33. LI, L., NI, J., ZHU, Z. & ZUO, X. 2023c. Simultaneous ammonium and phosphate removal with Mg-loaded chitosan carbonized microsphere: Influencing factors and removal mechanism. Environ

Res, 228, 115850.

34. LI, R., WANG, B., NIU, A., CHENG, N., CHEN, M., ZHANG, X., YU, Z. & WANG, S. 2022b. Application of biochar immobilized microorganisms for pollutants removal from wastewater: A review. Sci Total Environ, 837, 155563.
35. LIANG, H., WANG, W., LIU, H., DENG, X., ZHANG, D., ZOU, Y. & RUAN, X. 2023. Porous MgO-modified biochar adsorbents fabricated by the activation of Mg(NO(3))(2) for phosphate removal: Synergistic enhancement of porosity and active sites. Chemosphere, 324, 138320.
36. LIANG, Y., ZHANG, Q., LI, S., FEI, J., ZHOU, J., SHAN, S., LI, Z., LI, H. & CHEN, S. 2022. Highly efficient removal of quinolones by using the easily reusable MOF derived-carbon. J Hazard Mater, 423, 127181.
37. LIN, J., SUN, S., XU, D., CUI, C., MA, R., LUO, J., FANG, L. & LI, H. 2022. Microwave directional pyrolysis and heat transfer mechanisms based on multiphysics field stimulation: Design porous biochar structure via controlling hotspots formation. Chemical Engineering Journal, 429.
38. LIU, B., GAI, S., LAN, Y., CHENG, K. & YANG, F. 2022. Metal-based adsorbents for water eutrophication remediation: A review of performances and mechanisms. Environ Res, 212, 113353.
39. LIU, X., WEI, J., HOU, L., ZHU, Y., WU, Y., XING, L., ZHANG, Y. & LI, J. 2021. Feasibility of nanoscale zerovalent iron-loaded sediment-based biochar (nZVI-SBC) for simultaneous removal of nitrate and phosphate: high selectivity toward dinitrogen and synergistic mechanism. Environ Sci Pollut Res Int, 28, 37448-37458.
40. LIU, Y., WENG, Z., HAN, B., GUO, Z., TIAN, H., TANG, Y., CAI, Y. & YANG, Z. 2023a. Recent studies on the comprehensive application of biochar in multiple environmental fields. Journal of Cleaner Production, 421.
41. LIU, Y., ZHONG, D., XU, Y., CHANG, H., DONG, L., HAN, Z., LI, J. & ZHONG, N. 2023b. Adsorption of phosphate in water by La/Al bimetallic-organic frameworks-chitosan composite with wide adaptable pH range. Journal of Environmental Chemical Engineering, 11.
42. LUO, Q., WEI, J., GUO, Z. & SONG, Y. 2024. Adsorption and immobilization of phosphorus from water and sediments using a lanthanum-modified natural zeolite: Performance, mechanism and effect. Separation and Purification Technology, 329.
43. LUO, X., HUANG, Z., LIN, J., LI, X., QIU, J., LIU, J. & MAO, X. 2020. Hydrothermal carbonization of sewage sludge and in-situ preparation of hydrochar/MgAl-layered double hydroxides composites for adsorption of Pb(II). Journal of Cleaner Production, 258.
44. LYU, H., GAO, B., HE, F., ZIMMERMAN, A. R., DING, C., TANG, J. & CRITTENDEN, J. C. 2018. Experimental and modeling investigations of ball-milled biochar for the removal of aqueous methylene blue. Chemical Engineering Journal, 335, 110-119.
45. MANMEEN, A., KONGJAN, P., PALAMANIT, A. & JARIYABOON, R. 2023. Biochar and pyrolysis liquid production from durian peel by using slow pyrolysis process: Regression analysis, characterization, and economic assessment. Industrial Crops and Products, 203.
46. MANYATSHE, A., CELE, Z. E. D., BALOGUN, M. O., NKAMBULE, T. T. I. & MSAGATI, T. A. M. 2022. Chitosan modified sugarcane bagasse biochar for the adsorption of inorganic phosphate ions from aqueous solution. Journal of Environmental Chemical Engineering, 10.
47. MOMINA, SHAHADAT, M. & ISAMIL, S. 2018. Regeneration performance of clay-based adsorbents for the removal of industrial dyes: a review. RSC Adv, 8, 24571-24587.
48. PAPADOPOULOU, E., GONZáLEZ, M. C., REIF, D., AHMED, A., TSAPEKOS, P., ANGELIDAKI, I. & HARASEK, M. 2023. Separation of lactic acid from fermented residual

resources using membrane technology. Journal of Environmental Chemical Engineering, 11.

49. PRIYA, E., KUMAR, S., VERMA, C., SARKAR, S. & MAJI, P. K. 2022. A comprehensive review on technological advances of adsorption for removing nitrate and phosphate from waste water. Journal of Water Process Engineering, 49.
50. QIU, B., SHAO, Q., SHI, J., YANG, C. & CHU, H. 2022. Application of biochar for the adsorption of organic pollutants from wastewater: Modification strategies, mechanisms and challenges. Separation and Purification Technology, 300.
51. QU, J., MENG, Q., PENG, W., SHI, J., DONG, Z., LI, Z., HU, Q., ZHANG, G., WANG, L., MA, S. & ZHANG, Y. 2023. Application of functionalized biochar for adsorption of organic pollutants from environmental media: Synthesis strategies, removal mechanisms and outlook. Journal of Cleaner Production, 423.
52. RAJPUT, M. K., HAZARIKA, R. & SARMA, D. 2023. Zerovalent iron decorated tea waste derived porous biochar [ZVI@TBC] as an efficient adsorbent for Cd(II) and Cr(VI) removal. Journal of Environmental Chemical Engineering, 11.
53. REIF, D., WEISZ, L., KOBSIK, K., SCHAAR, H., SARACEVIC, E., KRAMPE, J. & KREUZINGER, N. 2023. Adsorption/precipitation prototype agent for simultaneous removal of phosphorus and organic micropollutants from wastewater. Journal of Environmental Chemical Engineering, 11.
54. RUSMIN, R., SARKAR, B., MUKHOPADHYAY, R., TSUZUKI, T., LIU, Y. & NAIDU, R. 2022. Facile one pot preparation of magnetic chitosan-palygorskite nanocomposite for efficient removal of lead from water. J Colloid Interface Sci, 608, 575-587.
55. SHAKOOR, M. B., YE, Z. L. & CHEN, S. 2021. Engineered biochars for recovering phosphate and ammonium from wastewater: A review. Sci Total Environ, 779, 146240.
56. SHEN, X., LI, H., ZHAO, Z., LI, X., LIU, K. & GAO, X. 2022. Imaging of liquid temperature distribution during microwave heating via thermochromic metal organic frameworks. International Journal of Heat and Mass Transfer, 189.
57. SHI, W., FU, Y., JIANG, W., YE, Y., KANG, J., LIU, D., REN, Y., LI, D., LUO, C. & XU, Z. 2019. Enhanced phosphate removal by zeolite loaded with Mg–Al–La ternary (hydr)oxides from aqueous solutions: Performance and mechanism. Chemical Engineering Journal, 357, 33-44.
58. SICILIANO, A., CURCIO, G. M., LIMONTI, C., MASI, S. & GRECO, M. 2021. Methylene blue adsorption on thermo plasma expanded graphite in a multilayer column system. J Environ Manage, 296, 113365.
59. SONG, W., ZHANG, L., GUO, B., SUN, Q., YU, Z., XU, X., ZHAO, Y. & YAN, L. 2023. Quaternized straw supported by La(OH)3 nanoparticles for highly-selective removal of phosphate in presence of coexisting anions: Synergistic effect and mechanism. Separation and Purification Technology, 324.
60. TOŃSKI, M., PASZKIEWICZ, M., DOŁŻONEK, J., FLEJSZAR, M., BIELICKA-GIEŁDOŃ, A., STEPNOWSKI, P. & BIAŁK-BIELIŃSKA, A. 2021. Regeneration and reuse of the carbon nanotubes for the adsorption of selected anticancer drugs from water matrices. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 618.
61. WANG, H. S.-H. & YAO, Y. 2023. Machine learning for sustainable development and applications of biomass and biomass-derived carbonaceous materials in water and agricultural systems: A review. Resources, Conservation and Recycling, 190.
62. WANG, Z., HUANG, Z., ZHENG, B., WU, D. & ZHENG, S. 2022. Efficient removal of phosphate

and ammonium from water by mesoporous tobermorite prepared from fly ash. Journal of Environmental Chemical Engineering, 10.

63. WANG, Z., SHEN, D., SHEN, F. & LI, T. 2016. Phosphate adsorption on lanthanum loaded biochar. Chemosphere, 150, 1-7.
64. WEI, Z., LI, H., JIA, M. & LIN, T. 2023. NaOH–ball-milled co-modified magnetic biochar and its oil adsorption properties. Particuology, 83, 40-49.
65. WU, J., YANG, J., HUANG, G., XU, C. & LIN, B. 2020. Hydrothermal carbonization synthesis of cassava slag biochar with excellent adsorption performance for Rhodamine B. Journal of Cleaner Production, 251.
66. XI, H., ZHANG, X., HUA ZHANG, A., GUO, F., YANG, Y., LU, Z., YING, G. & ZHANG, J. 2022. Concurrent removal of phosphate and ammonium from wastewater for utilization using Mg-doped biochar/bentonite composite beads. Separation and Purification Technology, 285.
67. XIN, Y., CAO, H., YUAN, Q. & WANG, D. 2017. Two-step gasification of cattle manure for hydrogen-rich gas production: Effect of biochar preparation temperature and gasification temperature. Waste Manag, 68, 618-625.
68. XU, C., FENG, Y., LI, H., YANG, Y., JIANG, S., WU, R., MA, R. & XUE, Z. 2023a. Adsorption of phosphorus from eutrophic seawater using microbial modified attapulgite - cleaner production, remove behavior, mechanism and cost-benefit analysis. Chemical Engineering Journal, 458.
69. XU, S., DENG, W., HU, M., CHEN, G., ZHOU, P., LI, F. & SU, Y. 2022. Preparation of activated sludge char through microwave-assisted one-step pyrolysis and activation for gaseous H2S removal. Chemical Engineering and Processing - Process Intensification, 181.
70. XU, Z., ZHANG, B., WANG, T., LIU, J., MEI, M., CHEN, S. & LI, J. 2023b. Environmentally friendly crab shell waste preparation of magnetic biochar for selective phosphate adsorption: Mechanisms and characterization. Journal of Molecular Liquids, 385.
71. YANG, B., HAN, F., BAI, Y., XIE, Z., SHI, T., WANG, J. & LI, Y. 2023. Phosphate removal performance and mechanism of magnesium–lanthanum-modified coal gasification coarse slag. Materials Today Sustainability, 22.
72. YU, J., CHANG, J. S., GUO, H., HAN, S. & LEE, D. J. 2023. Sodium ions removal by sulfuric acid-modified biochars. Environ Res, 235, 116592.
73. YUN, H., KIM, Y. J., KIM, S. B., YOON, H. J., KWAK, S. K. & LEE, K. B. 2022. Preparation of copper-loaded porous carbons through hydrothermal carbonization and ZnCl(2) activation and their application to selective CO adsorption: Experimental and DFT calculation studies. J Hazard Mater, 426, 127816.
74. ZHANG, L., FENG, M., ZHAO, D., LI, M., QIU, S., YUAN, M., GUO, C., HAN, W., ZHANG, K. & WANG, F. 2023a. La-Ca-quaternary amine-modified straw adsorbent for simultaneous removal of nitrate and phosphate from nutrient-polluted water. Separation and Purification Technology, 304.
75. ZHANG, M., SONG, G., GELARDI, D. L., HUANG, L., KHAN, E., MASEK, O., PARIKH, S. J. & OK, Y. S. 2020a. Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water. Water Res, 186, 116303.
76. ZHANG, W., TAN, X., GU, Y., LIU, S., LIU, Y., HU, X., LI, J., ZHOU, Y., LIU, S. & HE, Y. 2020b. Rice waste biochars produced at different pyrolysis temperatures for arsenic and cadmium abatement and detoxification in sediment. Chemosphere, 250, 126268.
77. ZHANG, X., LIU, Z. & QU, D. 2023b. Proof-of-Concept study of ion-exchange method for the recycling of LiFePO(4) cathode. Waste Manag, 157, 1-7.

78. ZHANG, X., MA, X., YU, Z., YI, Y., HUANG, Z. & LU, C. 2022. Preparation of high-value porous carbon by microwave treatment of chili straw pyrolysis residue. Bioresour Technol, 360, 127520.
79. ZHANG, Y., WAN, Y., ZHENG, Y., YANG, Y., HUANG, J., CHEN, H., QUAN, G. & GAO, B. 2023c. Potassium permanganate modification of hydrochar enhances sorption of Pb(II), Cu(II), and Cd(II). Bioresour Technol, 386, 129482.
80. ZHANG, Y., ZHENG, Y., YANG, Y., HUANG, J., ZIMMERMAN, A. R., CHEN, H., HU, X. & GAO, B. 2021. Mechanisms and adsorption capacities of hydrogen peroxide modified ball milled biochar for the removal of methylene blue from aqueous solutions. Bioresour Technol, 337, 125432.
81. ZHENG, X., MA, X., HUA, Y., LI, D., XIANG, J., SONG, W. & DONG, J. 2021. Nitric acid-modified hydrochar enhance Cd(2+) sorption capacity and reduce the Cd(2+) accumulation in rice. Chemosphere, 284, 131261.
82. ZHI, Y., PATERSON, A. R., CALL, D. F., JONES, J. L., HESTERBERG, D., DUCKWORTH, O. W., POITRAS, E. P. & KNAPPE, D. R. U. 2022. Mechanisms of orthophosphate removal from water by lanthanum carbonate and other lanthanum-containing materials. Sci Total Environ, 820, 153153.
83. ZHOU, Y., SHEN, C., XIANG, L., XUE, Y., LU, M. & WANG, T. 2023. Facile synthesis of magnetic biochar from an invasive aquatic plant and basic oxygen furnace slag for removal of phosphate from aqueous solution. Biomass and Bioenergy, 173.
84. ZHUO, S. N., DAI, T. C., REN, H. Y. & LIU, B. F. 2022. Simultaneous adsorption of phosphate and tetracycline by calcium modified corn stover biochar: Performance and mechanism. Bioresour Technol, 359, 127477.